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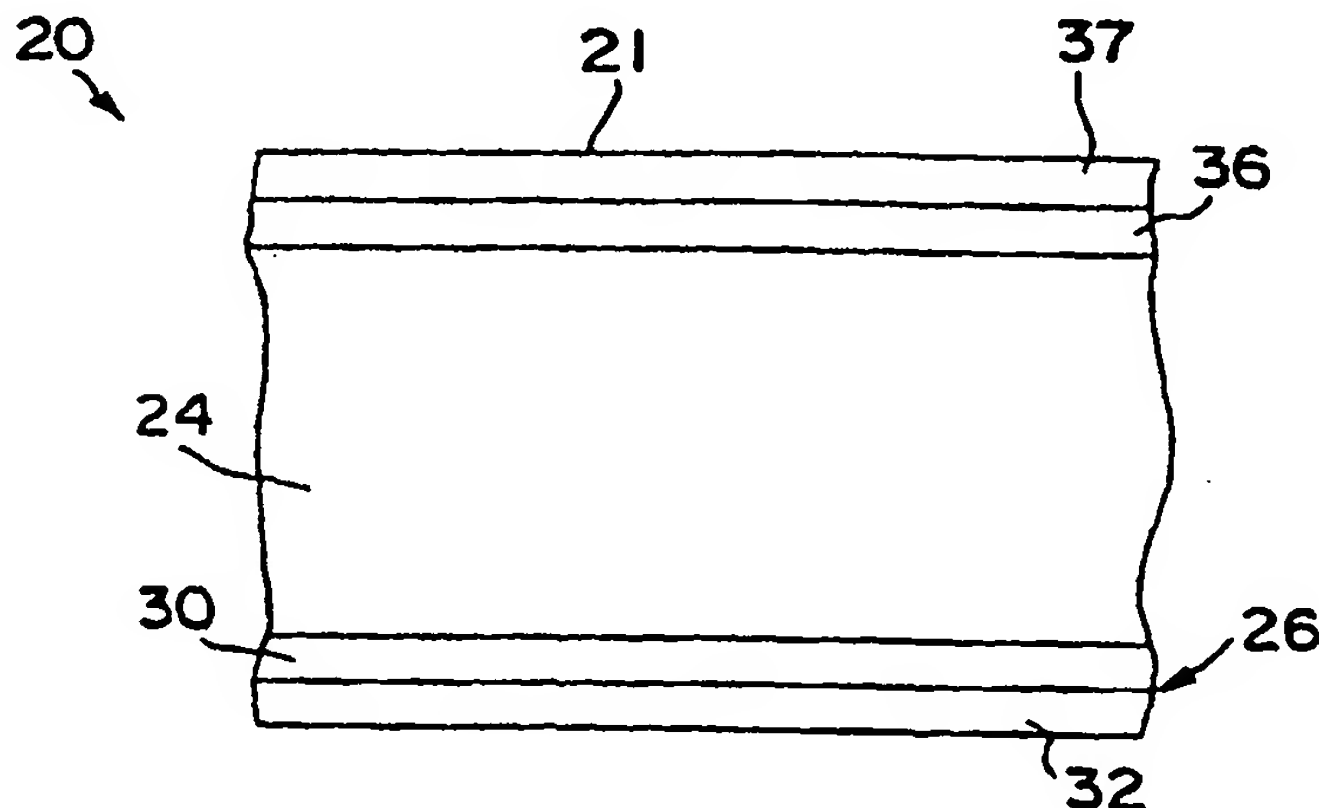
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(54) Title: ELASTOMERIC ARTICLES HAVING IMPROVED CHEMICAL RESISTANCE



(57) Abstract: An elastomeric article (e.g., glove, condom, etc.) that includes a chemical protection layer that will not substantially dissolve when applied with certain chemicals or solvents, such as methyl methacrylate, is provided. The chemical protection layer contains at least one crosslinked, modified silicone elastomer. For example, in one embodiment, the modified silicone chemical protection layer covers the outer surface of a styrene-ethylene-butylene-styrene (S-EB-S) block copolymer substrate body to impart relative chemical resistance to the resulting elastomeric article.

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## ELASTOMERIC ARTICLES HAVING IMPROVED CHEMICAL RESISTANCE

### Background of the Invention

Elastomeric articles, such as gloves, are often formed from synthetic  
5 polymers. Unfortunately, one problem sometimes associated with the formation of  
elastomeric articles from some types of synthetic polymers is that they tend to  
dissolve when contacted with certain chemicals or solvents. The dissolution of the  
elastomeric polymer may be especially problematic when used in certain fields,  
such as in the medical or automotive field. For example, a surgeon often wears  
10 elastomeric gloves during a procedure to protect the patient and surgeon from the  
possible spread of infection or disease. During the procedure, the surgeon may  
be required to utilize various chemicals or solvents, such as bone cement, that  
may undesirably dissolve the elastomeric polymer forming the glove, thereby  
exposing the surgeon's skin.

15 As such, a need currently exists for an improved elastomeric article that is  
relatively resistant to various types of chemicals or solvents.

### Summary of the Invention

In accordance with one embodiment of the present invention, an  
elastomeric article (e.g., glove, condom, etc.) is disclosed that comprises a  
20 substrate body including a layer made of an elastomeric material and a chemical  
protection layer covering the outside surface of the substrate body. The chemical  
protection layer includes at least one modified silicone elastomer that has been  
crosslinked. For example, in one embodiment, the modified silicone elastomer is  
selected from the group consisting of phenyl-modified silicones, vinyl-modified  
25 silicones, methyl-modified silicones, fluoro-modified silicones, alkyl-modified  
silicones, alkoxy-modified silicones, alkylamino-modified silicones, and  
combinations thereof.

The substrate body, as indicated above, contains an elastomeric material.  
In some instances, the elastomeric material of the substrate body is selected from  
30 the group consisting of styrene-ethylene-butylene-styrene block copolymers,  
styrene-isoprene-styrene block copolymers, styrene-polybutadiene-styrene block

copolymers, styrene-isoprene block copolymers, styrene-butadiene block copolymers, natural rubber latex, nitrile rubbers, isoprene rubbers, chloroprene rubbers, polyvinyl chlorides, silicone rubbers, and combinations thereof. For example, in one embodiment, the elastomeric material of the substrate body contains at least one styrene-ethylene-butylene-styrene triblock copolymer.

Besides the layers mentioned above, the elastomeric article may also contain other layers. In one embodiment, for instance, the elastomeric article can contain a donning layer overlying the inside surface of the substrate body. If desired, a lubricant layer may also overlay the inside surface of the donning layer.

In accordance with another embodiment of the present invention, a method for forming an elastomeric article (e.g., glove, condom, etc.) is disclosed. In particular, the method includes furnishing a liquid solution comprising a modified silicone elastomer and a solvent. A former having the shape of the elastomeric article is dipped into the liquid solution and withdrawn therefrom. The solvent is then evaporated from the liquid solution present on the former so that a modified silicone elastomer film is formed thereon. To induce crosslinking in the modified silicone elastomer, it is heated, such as to a temperature of from about 200°F to about 400°F, and in some embodiments, from about 200°F to about 350°F.

Various properties of the chemical protection layer may be varied to achieve an elastomeric article having certain characteristics. For example, the solids content of the uncrosslinked modified silicone elastomer can be from about 5% to about 40%, and in some embodiments, from about 10% to about 35%. Furthermore, the uncrosslinked modified silicone elastomer can have a viscosity of from about 300 centipoise to about 7000 centipoise, and in some embodiments, from about 600 centipoise to about 4000 centipoise. Moreover, the modified silicone elastomer film can have a thickness of from about 0.001 millimeters to about 0.4 millimeters, in some embodiments, from about 0.01 millimeters to about 0.30 millimeters, and in some embodiments, from about 0.01 millimeters to about 0.20 millimeters.

The method can also include dipping the crosslinked, modified silicone-coated former into a liquid solution of an elastomeric material (e.g., styrene-

ethylene-butylene-styrene) to form the substrate body.

In some embodiments, the former is further dipped into a liquid solution to apply a donning layer on the inside surface of the substrate body.

Other features and aspects of the present invention are discussed in greater detail below.

### **Brief Description of the Drawings**

A full and enabling disclosure of the present invention, including the best mode thereof, directed to one of ordinary skill in the art, is set forth in the specification, which makes reference to the appended drawings, in which:

Fig. 1 is a perspective view of one embodiment of an elastomeric glove made according to the invention;

Fig. 2 is a cross-sectional view of the glove illustrated in Fig. 1 taken along a line 2-2; and

Fig. 3 is a block flow diagram illustrating one embodiment of a method for forming an elastomeric article of the present invention.

Repeat use of reference characters in the present specification and drawings is intended to represent the same or analogous features or elements of the invention.

### **Detailed Description of Representative Embodiments**

Reference now will be made in detail to various embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations.

In general, the present invention is directed to an elastomeric article that includes a chemical protection layer that will not substantially dissolve when

contacted with certain chemicals or solvents, such as bone cement. The chemical protection layer contains at least one crosslinked, modified silicone elastomer. For example, in one embodiment, the modified silicone chemical protection layer covers the outer surface of a styrene-ethylene-butylene-styrene (S-EB-S) block copolymer substrate body to impart relative chemical resistance to the resulting elastomeric article.

Any of a variety of elastomeric articles can be provided with improved chemical resistance properties in accordance with the present invention. For example, gloves and condoms, as well as medical devices, such as dilatation balloons, inflatable cuffs, external catheters, catheter balloons, instrument covers, and the like, can be formed according to the present invention. In addition, it should also be understood that other types of elastomeric articles may also be formed according to the present invention. For example, elastomeric materials often used in automotive applications, such as flexible rubber hoses, can also be formed with the crosslinked modified silicone elastomer in accordance with the present invention.

Referring to Figs. 1-2, for example, one embodiment of an elastomeric glove 20 is illustrated that can be placed on the hand of a user 22. The glove 20 includes a substrate body 24 having the basic shape of the glove. The substrate body 24 can generally be formed from any of a variety of natural and/or synthetic elastomeric materials known in the art. For instance, some examples of suitable elastomeric materials include, but are not limited to, S-EB-S (styrene-ethylene-butylene-styrene) block copolymers, S-I-S (styrene-isoprene-styrene) block copolymers, S-B-S (styrene-butadiene-styrene) block copolymers, S-I (styrene-isoprene) block copolymers, S-B (styrene-butadiene) block copolymers, natural rubber latex, nitrile rubbers, isoprene rubbers, chloroprene rubbers, polyvinyl chlorides, silicone rubbers, and combinations thereof. Other suitable elastomeric materials that can be used to form the substrate body 24 may be described in U.S. Patent No. 6,306,514 to Weikel, et al., which is incorporated herein in its entirety by reference thereto for all purposes.

In one particular embodiment, the substrate body 24 contains at least one



elastomeric block copolymer. Some S-EB-S block copolymers and methods for forming solutions thereof are described in U.S. Patent Nos. 5,112,900 to Buddenhagen, et al.; 5,407,715 to Buddenhagen, et al.; 5,900,452 to Plamthottam; and 6,288,159 to Plamthottam, which are incorporated herein in their entirety by reference thereto for all purposes.

The polystyrene end blocks of S-EB-S block copolymers utilized in the present invention typically have a weight average molecular weight of at least about 15,000 Daltons, and in some embodiments, from about 18,000 to about 20,000 Daltons. Moreover, the polystyrene end blocks of the block copolymers typically constitute from about 25% to about 35% by weight of the total weight of the S-EB-S polymer, which is generally from about 50,000 to about 300,000 Daltons. When utilizing such a weight average molecular weight of the polystyrene end blocks, the resulting elastomeric films can exhibit superior strength properties and have limited crack formation during drying and fusion.

If desired, mixtures of two or more S-EB-S copolymers may be utilized. In some instances, for example, two S-EB-S copolymers are utilized in which each block copolymer constitutes from about 40% to about 60% by weight of the mixture. In one embodiment, the first S-EB-S block copolymer has a solution viscosity of about 6500 cps at 25% by weight of copolymer in toluene (at 77°F) and the second S-EB-S block copolymer has a solution viscosity of about 2000 cps at 10% by weight of copolymer in toluene (at 77°F).

The use of S-EB-S block copolymer(s) in the substrate body 24 can generally provide a number of benefits. For example, elastomers based upon the S-EB-S block elastomeric block copolymers are substantially resistant to attack by ozone or by other oxidative conditions. Moreover, the mechanical properties of the S-EB-S block copolymers may be selected to provide the desirable combination of tensile strength, elasticity, and tactility utilized in some applications.

The structure, properties, and some applications of some S-EB-S elastomers are disclosed in U.S. Pat. Nos. 3,485,787; 3,830,767; 4,006,116; 4,039,629; 4,041,103; 4,386,179; 4,481,323; 4,511,354; and 4,613,640, which are incorporated herein in their entirety by reference thereto for all purposes.

Some commercially available examples of S-EB-S block copolymers, such as described above, include, but are not limited to, Kraton® G1650, Kraton® G1651, Kraton® G1652, which are available from Kraton Polymers of Houston, Texas. Kraton® G1650 is an S-EB-S block copolymer having a styrene/central block ratio of 28/72 and a Brookfield Viscosity in toluene solution (20% concentration by weight) at 77°F of 1500 centipoise. Kraton® G1651 is an S-EB-S block copolymer having a styrene/central block ratio of 33/67 and a Brookfield Viscosity in toluene solution (20% concentration by weight) at 77°F of 2000 centipoise. Kraton® G1652 is an S-EB-S block copolymer having a styrene/central block ratio of 29/71 and a Brookfield Viscosity in toluene solution (20% concentration by weight) at 77°F of 550 centipoise.

The S-EB-S block copolymer(s) may optionally have end-block compatible resins added to the polystyrene end blocks. The added end-block compatible resin increases the glass transition temperature ( $T_g$ ) of the S-EB-S block copolymer. The increased  $T_g$  allows the final products to be used at higher temperatures. For instance, one suitable example of such an end-block compatible resin is poly alpha methyl styrene.

A plasticizer (e.g., an oil) can also be mixed with the S-EB-S block copolymer(s) to enhance the resulting properties of the elastomeric article. For example, in one embodiment, the plasticizer can include a mineral oil, such as a refined petroleum paraffinic hydrocarbon oil, which is described in Entries 6971 and 6972 of the Merck Index, Eighth Edition. The plasticizer can generally be mixed with the S-EB-S block copolymers in any desired amount. For example, in some embodiments, the plasticizer comprises between about 30 to about 80 parts by weight of the total mass of the S-EB-S block copolymer(s).

Besides containing a plasticizer, the S-EB-S block copolymer(s) can also be mixed with a solvent. In particular, S-EB-S block copolymers are often provided as a solid. In such instances, a solvent can be utilized to enhance the ability of the copolymers to be used in a dipping process, as described in more detail below. Any solvent capable of dissolving one or more S-EB-S block copolymers can generally be used in the present invention. For example, some suitable solvents

that can be used include toluene and cyclohexane. Once mixed with the copolymer(s), the ingredients can be mixed for a sufficient time to reach a homogeneous solution and then filtered to remove any undesired particulate matter.

5           Regardless of the particular material used to form the substrate body 24, the glove 20 also includes a chemical protection layer 36 that covers the outer surface of the substrate body 24 during use. Thus, for example, the chemical protection layer 36 can form an environment-exposed surface 21 of the glove, or  
10           can be positioned between the substrate body 24 and an additional layer that forms the environment-exposed surface 21. The chemical protection layer 36 contains a modified silicone elastomer that is crosslinked to impart chemical resistance to the glove 20. As used herein, the term "modified silicone" generally refers to a broad family of synthetic polymers that have a repeating silicon-oxygen backbone with organic groups attached to the backbone (pendant and/or  
15           terminating). For instance, some suitable silicones that can be used in the present invention include, but are not limited to, phenyl-modified silicones, vinyl-modified silicones, methyl-modified silicones, fluoro-modified silicones, alkyl-modified silicones, alkoxy-modified silicones, alkylamino-modified silicones, and combinations thereof.

20           Some suitable phenyl-modified silicones include, but are not limited to, dimethyldiphenylpolysiloxane copolymers; dimethyl, methylphenylpolysiloxane copolymers; polymethylphenylsiloxane; and methylphenyl, dimethylsiloxane copolymers. Phenyl modified silicones that have a relatively low phenyl content (less than about 50 mole %) may be particularly effective in the present invention.  
25           For example, the phenyl-modified silicone can be a diphenyl-modified silicone, such as a diphenylsiloxane-modified dimethylpolysiloxane.

          For most applications, the phenyl-modified silicones contain phenyl units in an amount from about 0.5 mole % to about 50 mole %, in some embodiments in an amount less than about 25 mole %, and in some embodiments, in an amount  
30           less than about 15 mole %. In one particular embodiment, a diphenylsiloxane-modified dimethylpolysiloxane can be used that contains diphenylsiloxane units in



an amount less than about 5 mole %, and particularly in an amount less than about 2 mole %. The diphenylsiloxane-modified dimethylpolysiloxane can be synthesized by reacting diphenylsiloxane with dimethylsiloxane.

As indicated above, fluoro-modified silicones can also be used in the present invention. For instance, one suitable fluoro-modified silicone that can be used is a trifluoropropyl modified polysiloxane, such as a trifluoropropylsiloxane modified dimethylpolysiloxane. A trifluoropropylsiloxane modified dimethylpolysiloxane can be synthesized by reacting methyl, 3,3,3 trifluoropropylsiloxane with dimethylsiloxane.

The fluoro-modified silicones can contain from about 5 mole % to about 95 mole %, and in some embodiments, from about 40 mole % to about 60 mole % of fluoro groups, such as trifluoropropylsiloxane units. In one embodiment, a trifluoropropylsiloxane-modified dimethylpolysiloxane is used that contains 50 mole % trifluoropropylsiloxane units.

Besides the above-mentioned modified silicone elastomers, other modified silicone elastomers may also be utilized in the present invention. For instance, some suitable vinyl-modified silicones include, but are not limited to, vinyl dimethyl terminated polydimethylsiloxanes; vinyl methyl, dimethylpolysiloxane copolymers; vinyl dimethyl terminated vinyl methyl, dimethylpolysiloxane copolymers; divinyl methyl terminated polydimethylsiloxanes; polydimethylsiloxane, mono vinyl, mono n-butyl dimethyl terminated; and vinyl phenyl methyl terminated polydimethylsiloxanes. Further, some methyl-modified silicones that can be used include, but are not limited to, dimethyl hydro terminated polydimethylsiloxanes; methyl hydro, dimethylpolysiloxane copolymers; methyl hydro terminated methyloctyl siloxane copolymers; and methyl hydro, phenyl methyl siloxane copolymers.

The particular elastomers described above are meant to include hetero- or co-polymers formed from polymerization or copolymerization of dimethylsiloxane cyclics and diphenylsiloxane cyclics or trifluoropropylsiloxane cyclics with appropriate endcapping units. Thus, for example, the terms "diphenyl modified dimethylpolysiloxanes" and "copolymers of diphenylpolysiloxane and

dimethylpolysiloxane" may be used interchangeably.

If desired, the chemical protection layer 36 can be formed from two or more separate components. When utilized, the separate components may contain the same or different types of modified silicone elastomers. For example, in one embodiment, the chemical protection layer 36 contains two components, designated herein as part "A" and "B". In one embodiment, part A contains a polydimethylsiloxane that is vinyl and methyl terminated. A platinum catalyst is also included that contains a complex of platinum with vinyl-containing oligosiloxanes (complex of platinum and divinyltetramethyldisiloxane with typical levels of active platinum of 5 to 50 parts per million). Part B is essentially identical to part A, except that it also includes a crosslinker and crosslinking inhibitor. The crosslinker can be, for example, polydimethylsiloxane with hydrogen on the siloxane chain, commonly called methyl hydrogen. The crosslinker concentration can vary from about 0.3 to about 4 parts per hundred parts of the mass of polydimethylsiloxane. The crosslinking inhibitor can, for example, contain an oligosiloxane with high concentration of vinyl-containing substituents of any of the class of compounds known as acetylinic alcohols. For example, one suitable crosslinking inhibitor is tetravinyl tetramethyl cyclotetrasiloxane. The inhibitor may be used in concentrations as low as 0.02 parts per hundred parts to as high as 0.5 parts per hundred parts. In forming the outer layer 36, parts A and B are mixed together prior to dipping in a 1:1 ratio by weight.

Some commercially available diphenyl modified dimethylsilicones, such as described above, can be obtained from NuSil Technologies under various trade names including MED 6400, MED 10-6400, MED 6600, MED 10-6600, MED 6640, and MED 10-6640. For example, the following Table provides some physical properties for MED 6400, MED 6600, and MED 6640.

	<u>MED 6400*</u>	<u>MED 6600*</u>	<u>MED 6640*</u>
Viscosity, cP	600	300	7000
Solvent	Xylene	Xylene	Xylene
Solids Content	35	35	25
Cure System	Platinum-based	Platinum-based	Platinum-based

\*MED 6400, 6600, and 6640 contain the same viscosity, solvent, solids content, and cure system as MED 10-6400, 10-6600, and 10-6640, respectively.

Other suitable modified silicone elastomers that can be used in the present invention are believed to be described in U.S. Patent Nos. 4,309,557 to Compton, et al.; 6,136,039 to Kristonsson, et al.; 6,160,151 to Compton, et al.; 6,243,938 to Lubrecht; and WO 01/41700, which are incorporated herein in their entirety by reference thereto for all purposes. Moreover, the modified silicone elastomers used in the present invention may also contain fillers, such as reinforcing silica; processing aids; additives; pigments; and the like, as is conventional in the art.

The solids content and/or viscosity of the chemical protection layer 36 can generally be varied to achieve the desired chemical resistance. For example, the modified silicone elastomer(s) used to form the chemical protection layer 36 can have a solids content of between about 5% to about 40%, and in some embodiments, between about 10% to about 35%. To lower the solids content of a commercially available modified silicone elastomer, for example, additional amounts of solvent can be utilized. Further, the viscosity of the modified silicone elastomer(s) used to form the chemical protection layer 36 can range from about 300 centipoise to about 7000 centipoise, and in some embodiments, from about 600 to about 4000 centipoise. By varying the solids content and/or viscosity of the chemical protection layer 36, the presence of the modified silicone elastomer in the glove can be controlled. For example, to form a glove with a higher level of chemical resistance, the modified silicone elastomer used in such layer can have a relatively high solids content and viscosity so that a greater percentage of the silicone is incorporated into the layer during the forming process. The thickness of the chemical protection layer 36 can also vary. For example, the thickness can range from about 0.001 millimeters to about 0.4 millimeters, in some embodiments, from about 0.01 millimeters to about 0.30 millimeters, and in some embodiments, from about 0.01 millimeters to about 0.20 millimeters.

Besides the chemical protection layer 36 and the substrate body 24, the glove 20 can also contain other layers. For example, as shown in Fig. 2, the glove 20 can contain a coating 26 that contacts the body of the user 22 during use. In this embodiment, the coating 26 includes a donning layer 30 overlying and contacting the substrate body 24 and a surfactant layer 32 overlying and

contacting the donning layer 30.

The donning layer 30 can contain any of a variety of different elastomeric polymers that are capable of facilitating donning of the glove. Some examples of suitable materials for the donning layer 30 include, but are not limited to, polybutadienes (e.g., syndiotactic 1,2 polybutadiene), polyurethanes, halogenated copolymers, and the like. For instance, in one embodiment, an unsaturated styrene-isoprene (SIS) having tri- or radial-blocks can be utilized. In some embodiments, the SIS block copolymer has a polystyrene end block content of from about 10% to about 20% by weight, and particularly from about 15% to about 18% by weight, of the total weight of the SIS block copolymer. Moreover, the molecular weight of the polystyrene end blocks is typically at least about 5,000 grams per mole. Some examples of suitable mid-block unsaturated SIS block copolymers include, but are not limited to, Kraton® D1107 available from Kraton Polymers and Vector® 511 and Vector® 4111 available from Dexco Polymers of Houston, Texas.

Another suitable donning material is 1,2 polybutadiene (e.g., syndiotactic 1,2 polybutadiene). In one embodiment, for example, the donning layer 30 is formed from a solution that contains from about 2% to about 7% by weight, and particularly from about 3% to about 4% by weight of 1,2 polybutadiene in a solvent (e.g., toluene). For instance, one suitable example of a polybutadiene material that can be dissolved in toluene to form a coating solution is "COMPATIBAG", which is available from Presto Products of Appleton, Wisconsin and contains syndiotactic 1,2 polybutadiene. The 1,2 polybutadiene can also be formed as an emulsion to be applied as the donning layer 30. In some embodiments, for example, the emulsion contains from about 5% to about 14% by weight, and particularly about 9% by weight of 1,2 polybutadiene in a surfactant mixture. In one embodiment, the surfactant mixture is sodium dioctyl sulfosuccinate in an amount from about 10 phr (parts per hundred rubber) to about 100 phr, and particularly 40 phr in water. Pre-dispersion can be achieved by dispersing the surfactant mixture and 1,2 polybutadiene solution using a mixer, such as a high shear mixture. In one embodiment, the pre-dispersion is then mixed for about 5



minutes in a rotor/stator (such as a Ross X Series) mixer to generate an average particle size of less than about 1 micrometer. The resulting emulsion can then be filtered and the solvent can be removed by vacuum distillation.

5 In addition, polyurethanes may also be utilized as a donning material. For example, in one embodiment, Hyslip 20022 (available from Noveon, Inc.) can be utilized. Hyslip 20022 contains 1-methyl-2-pyrrolidone and waterborne polyurethane. Other examples of donning materials that can be utilized in the donning layer 30 may be described in U.S. Patent No. 5,792,531 to Littleton, et al., which is incorporated herein in its entirety by reference thereto for all purposes.

10 A lubricant layer 32 can also overly the donning layer 30 to aid in donning the article when the user's body is either wet or dry. The lubricant layer 32, for example, can include a cationic (e.g., cetyl pyridinium chloride), an anionic (e.g., sodium lauryl sulfate), or a nonionic surfactant. For instance, in one embodiment, the lubricant layer 32 contains a quaternary ammonium compound, such as  
15 Verisoft BTMS (available from Goldschmidt Chemical Corp. of Dublin, Ohio) and a silicone emulsion (AF-60) obtained from General Electric Silicone. Verisoft BTMS contains behnlyl trimethyl sulfate and cetyl alcohol, while AF-60 contains polydimethylsiloxane, acetylaldehyde, and small percentages of emulsifiers. In another embodiment, the lubricant layer 32 contains a medical-grade silicone such  
20 as Dow Corning 365 silicone, which is believed to contain water, polydimethylsiloxane, octylphenoxy polyethoxy ethanol, propylene glycol, and polyethylene glycol sorbitan monolaurate.

Further, besides the above-mentioned layers, the glove 20 can also contain additional layers if desired. For example, in one embodiment, the glove 20  
25 contains a layer 37 that defines an environment-exposed surface 21 of the glove 20. Although optional, the layer 37 can be utilized to inhibit blocking between the layers and to facilitate stripping of the glove 20 from a former. For example, in one embodiment, the layer 37 can contain styrene-polybutadiene-styrene (S-B-S) or a polyurethane material. It should also be understood, however, that the chemical  
30 protection layer 36 can define the environment-exposed surface 21 of the glove 20. In such instances, the layer 37 may or may not be positioned between the



chemical protection layer 36 and the substrate body 24.

An elastomeric article made in accordance with the present invention can generally be formed using a variety of processes known in the art. In fact, any process capable of making an elastomeric article can be utilized in the present invention. For example, elastomeric article formation techniques can utilize dipping, spraying, chlorination, drying, curing, as well as any other technique known in the art. In this regard, referring to Fig. 3, one embodiment of a method of dip forming a glove will now be described in more detail. Although a batch process is described and shown herein, it should be understood that semi-batch and continuous processes may also be utilized in the present invention.

Initially, any well-known former, such as formers made from metals, ceramics, or plastics, is provided. Although glove-shaped formers are described herein, it should also be understood that formers having any other shape (e.g., condom-shaped) can be used in accordance with the present invention to form articles having different shapes. The former is dipped into a dip tank containing the modified silicone elastomer and solvent, such as xylene, water, etc. (illustrated as numeral 62). A high shear mixer is utilized for a sufficient time to reach a homogeneous solution prior to dipping. After dipping, the former is removed slowly from the dip tank, leaving a thin, uniform layer of the liquid silicone elastomer solution deposited onto the former. Once removed from the dip tank, the modified silicone-coated former is then dried to remove the solvent from the coating (illustrated as numeral 64). For example, in some embodiments, the modified silicone-coated former can be air dried at a temperature of from about 100°F to about 240°F.

Once dried, the former is then transferred to a curing station (e.g., oven) where the modified silicone is cured (illustrated as numeral 66). The curing station heats the modified silicone-coated former to a temperature sufficient to achieve the desired level of crosslinking. For example, in some embodiments, the curing station heats the modified silicone-coated former to a temperature ranging from about 200°F to about 400°F, and in some embodiments, from about 200°F to about 350°F. It should be understood that the curing station may also be used to

remove solvent from the chemical protection layer 36. In such instances, the modified silicone-coated former may not be dried before being transferred to the curing station. For example, the oven may be divided into two different zones with a former being conveyed through the zones of increasing temperature. One  
5 example is an oven having two zones with the first zone being dedicated primarily to drying and the second zone being dedicated primarily to curing. For example, the first zone can heat the former to about 220°F and the second zone can heat the former to about 350°F. When heated, the catalyst and crosslinking agent contained in the modified silicone coating of the former are used to crosslink the  
10 silicone by forming a bridge between silicone chains.

The dipping procedure is repeated as necessary so that the chemical protection layer 36 has the desired thickness. By way of example, the chemical protection layer 36 of a glove produced by dip forming can have a thickness of from about 0.01 millimeters to about 0.20 millimeters.

15 After the chemical protection layer 36 is formed, the entire former is then dipped into a dip tank containing the elastomeric polymer(s) used to form the substrate body 24 (illustrated as numeral 68). In one embodiment, for example, the former is dipped into a dip tank that contains at least one styrene-ethylene-butylene-styrene (S-EB-S) block copolymer, mineral oil, and a mutual solvent  
20 (e.g., toluene). The former is dipped into a liquid solution of the elastomer a sufficient number of times to build up the desired thickness on the form. By way of example, the substrate body 24 can have a thickness of from about 0.004 to about 0.012 inches. The glove is then allowed to dry. Methods for dip-forming S-EB-S layers are described in more detail in U.S. Patent Nos. 5,112,900 to  
25 Buddenhagen, et al. and 5,407,715 to Buddenhagen, et al.

The glove former is then dipped into a solution to form the donning layer 30 of the glove (illustrated as numeral 70). In one embodiment, for example, the glove former is dipped into a solution of 1,2 syndiotactic polybutadiene and toluene. The glove is then dried. Once the body of the glove is formed, such as  
30 described above, a bead roll station (not shown) can, in some embodiments, be utilized to impart a cuff to the glove. For instance, the bead roll station can contain

one or more bead rolls such that the former is indexed therethrough to be provided with cuffs. The formers may then be transferred to a stripping station (not shown).

The stripping station can involve automatic or manual removal of the gloves from the formers. For example, in one embodiment, the gloves are manually removed  
5 from each former by turning each glove inside-out as it is stripped from its corresponding former.

After being stripped, the gloves can then be chlorinated, if desired, using any known chlorination technique, such as described in U.S. Patent No. 5,792,531 to Littleton, et al. (illustrated as numeral 72). Upon chlorination, a lubricant can  
10 also be applied to the donning surface of the glove (illustrated as numeral 74). Specifically, the lubricant is applied to the donning surface of the glove using a sponge during a tumbling process. The glove is then dried in a hot air dryer.

Although various constructions and techniques for forming elastomeric articles have been described above, it should be understood that the present  
15 invention is not limited to any particular construction or technique for forming the article. For example, the layers described above may not be utilized in all instances. Additionally, other layers not specifically referred to above may be utilized in the present invention. Furthermore, the present invention is also not limited to any particular type of elastomeric article. For instance, condoms, flexible  
20 automotive hoses, and the like, may all be formed in accordance with the present invention with improved chemical resistance.

The present invention may be better understood with reference to the following example.

### **EXAMPLE**

25 The ability of an elastomeric article to be imparted with chemical resistance in accordance with the present invention was demonstrated. Initially, a glove-shaped former was dipped into a tank containing MED 10-6640, a modified silicone elastomer available from NuSil Technologies. After dipping, the former was removed from the silicone dip tank and allowed to dry in air at a temperature  
30 of 220°F to remove the solvent therefrom. Once dried, the modified silicone-coated former was then transferred to an oven, where it was crosslinked at a

temperature of 350°F. The resulting modified silicone layer had a thickness of about 0.10 millimeters.

Upon forming the modified silicone layer, the former was then dipped into a dip tank that contained an S-EB-S composition. Specifically, the S-EB-S composition contained 50% by weight Kraton® 1650 and 50% by weight Kraton® 1651. The S-EB-S composition was combined with mineral oil (67 parts per hundred rubber) and then dissolved in toluene so that the resulting solids content was about 20%. After dipping, the former was removed from the S-EB-S composition and dried in air at a temperature of 220°F. The thickness of the resulting glove was 0.27 millimeters.

Various glove samples formed in the manner described above were then tested to determine the chemical resistance of the glove. The solvents utilized to test the samples are set forth below in Table 1.

**Table 1. Solvents Tested**

Type	Trade Name	Manufacturer
Bone Cement	PALACOS R RADIOPAQUE <sup>1</sup>	Biomet Orthopedics (Washaw, Indiana)
	PALACOS R RADIOPAQUE <sup>2</sup>	Biomet Orthopedics (Washaw, Indiana)
Glue	SUPER GLUE	Elmer's Products (Columbus, Ohio)
	KRAZY GLUE	Elmer's Products (Columbus, Ohio)
	SUREHOLD PLASTIC SURGERY	Surehold, Inc. (Chicago, Illinois)
Tissue Adhesive	GLUSTITCH	Glustitch, Inc. (Delta, British Columbia, Canada)
	DERMABOND <sup>3</sup>	Ethicon, Inc. (Somerville, New Jersey)

<sup>1</sup> methylmethacrylate stabilized with hydroquinone, N,N-dimethyl-p-toluidine, and chlorophyll

<sup>2</sup> methyl methacrylate-methyl acrylate copolymer containing chlorophyll, benzoyl peroxide, and zirconium dioxide

<sup>3</sup> N-butylcyanoacrylate

For each solvent tested, a glove was first donned on one hand. The solvent was placed between the thumb, index, and middle finger, and a sweeping motion was then made for about 5 minutes (for bone cement) and about 10 minutes (for glue and tissue adhesive) with the thumb over the fingers. During the test period, the glove was visually inspected for irregularities, such as evidence of granular rubber particles, splits, cracks, dissolved rubber, increase in tackiness, discoloration, and the like.

In addition to the above-mentioned test, an additional test was also conducted for

the samples applied with glue and tissue adhesive. Specifically, a drop of the respective solvent was placed on each sample. The glove was then stretched in the location where the solvent was applied. After 24 hours, the glove was again stretched in the same location.

5           Upon inspection, no irregularities were visually observed in any of the glove samples tested.

10           While the invention has been described in detail with respect to the specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

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**WHAT IS CLAIMED IS:**

1. An elastomeric article that comprises:

a substrate body including a layer made of an elastomeric material, said substrate body having an inside surface and an outside surface; and

5 a chemical protection layer covering said outside surface of said substrate body, said chemical protection layer including at least one modified silicone elastomer that has been crosslinked.

2. An elastomeric article as defined in claim 1, wherein said modified silicone elastomer is selected from the group consisting of phenyl-modified  
10 silicones, vinyl-modified silicones, methyl-modified silicones, fluoro-modified silicones, alkyl-modified silicones, alkoxy-modified silicones, alkylamino-modified silicones, and combinations thereof.

3. An elastomeric article as defined in claim 2, wherein said modified silicone elastomer is selected from the group consisting of phenyl-modified  
15 silicones, vinyl-modified silicones, methyl-modified silicones, fluoro-modified silicones.

4. An elastomeric article as defined in claim 3, wherein said modified silicone elastomer contains a diphenyl modified dimethylsilicone.

5. An elastomeric article as defined in claim 1, wherein said chemical  
20 protection layer has a thickness of from about 0.01 millimeters to about 0.30 millimeters.

6. An elastomeric article as defined in claim 1, wherein said chemical protection layer has a thickness of from about 0.01 millimeters to about 0.20 millimeters.

7. An elastomeric article as defined in claim 1, wherein said chemical  
25 protection layer defines an outer surface of the elastomeric article.

8. An elastomeric article as defined in claim 1, wherein the elastomeric material of said substrate body is selected from the group consisting of styrene-ethylene-butylene-styrene block copolymers, styrene-isoprene-styrene block  
30 copolymers, styrene-polybutadiene-styrene block copolymers, styrene-isoprene block copolymers, styrene-butadiene block copolymers, natural rubber latex, nitrile

27. A method as defined in claim 21, wherein said uncrosslinked modified silicone elastomer has a solids content of from about 10% to about 35%.

28. A method as defined in claim 21, wherein said uncrosslinked modified silicone elastomer has a viscosity of from about 300 centipoise to about 7000 centipoise.

29. A method as defined in claim 21, wherein said uncrosslinked modified silicone elastomer has a viscosity of from about 600 centipoise to about 4000 centipoise.

30. A method as defined in claim 21, wherein said modified silicone elastomer film has a thickness of from about 0.01 millimeters to about 0.30 millimeters.

31. A method as defined in claim 21, wherein said modified silicone elastomer film has a thickness of from about 0.01 millimeters to about 0.20 millimeters.

32. A method as defined in claim 21, further comprising dipping said crosslinked, modified silicone-coated former into a liquid solution of an elastomeric material to form the substrate body.

33. A method as defined in claim 32, wherein said elastomeric material of said substrate body contains at least one styrene-ethylene-butylene-styrene triblock copolymer.

34. A method as defined in claim 32, further comprising dipping said former into a liquid solution to apply a donning layer on a surface of said substrate body.

35. A method as defined in claim 21, wherein the elastomeric article is a glove.

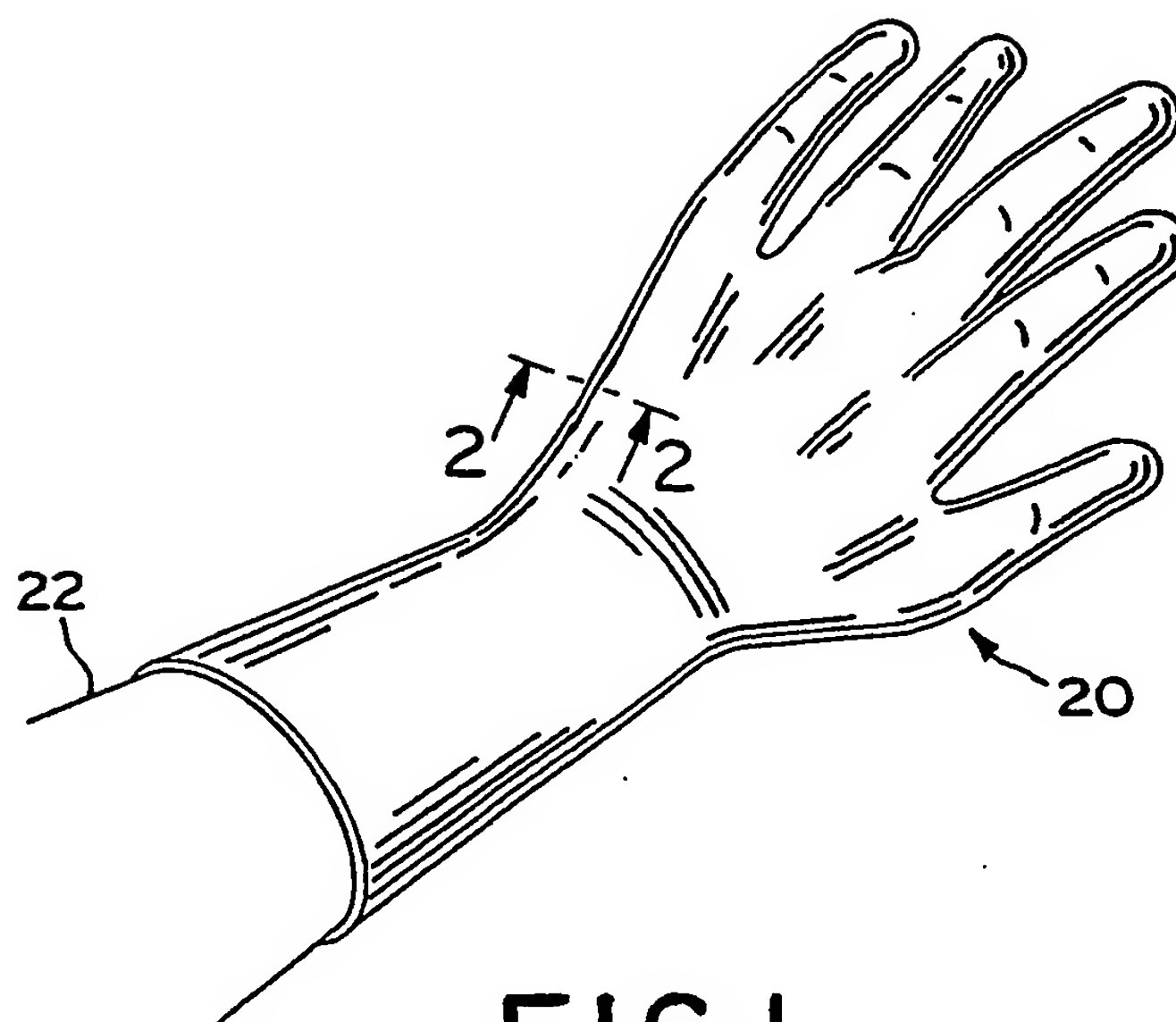


FIG. 1

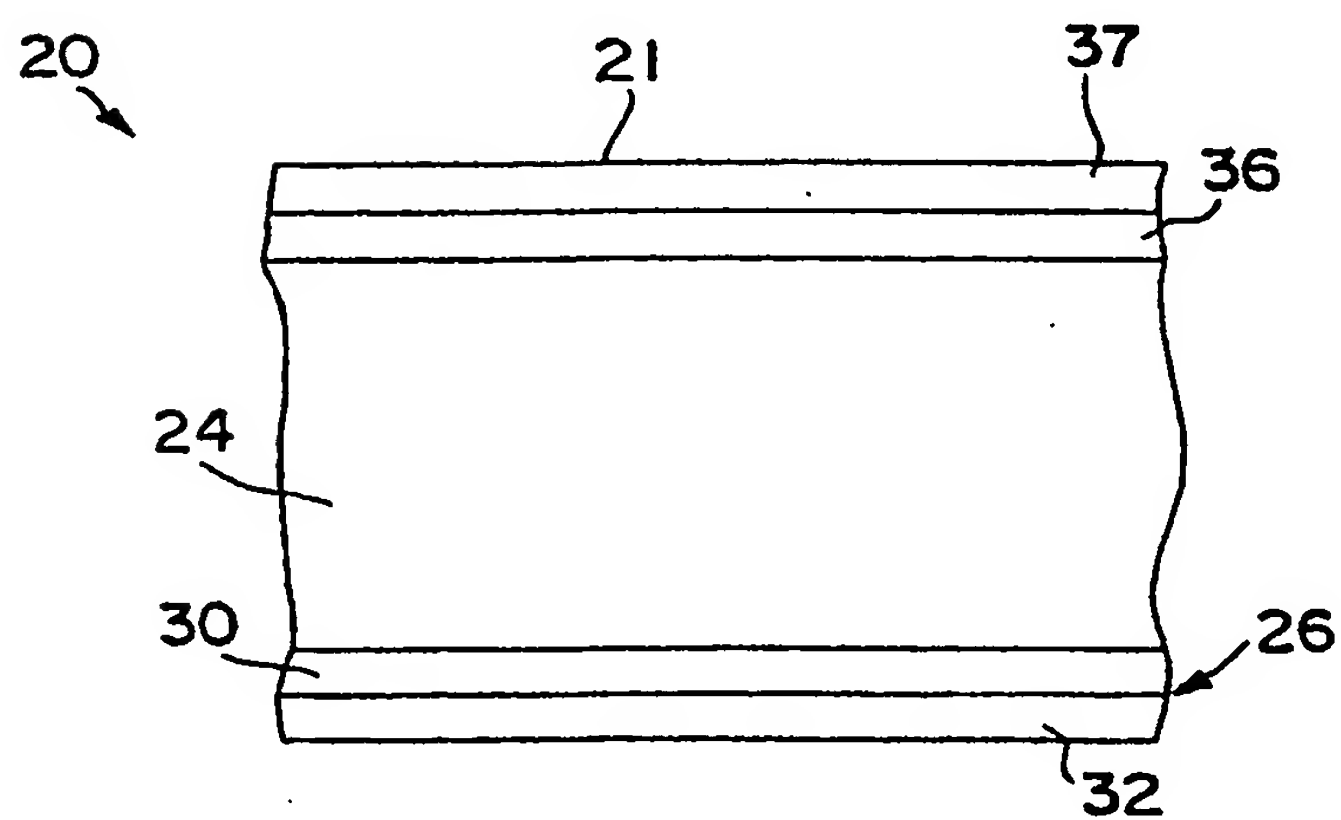


FIG. 2

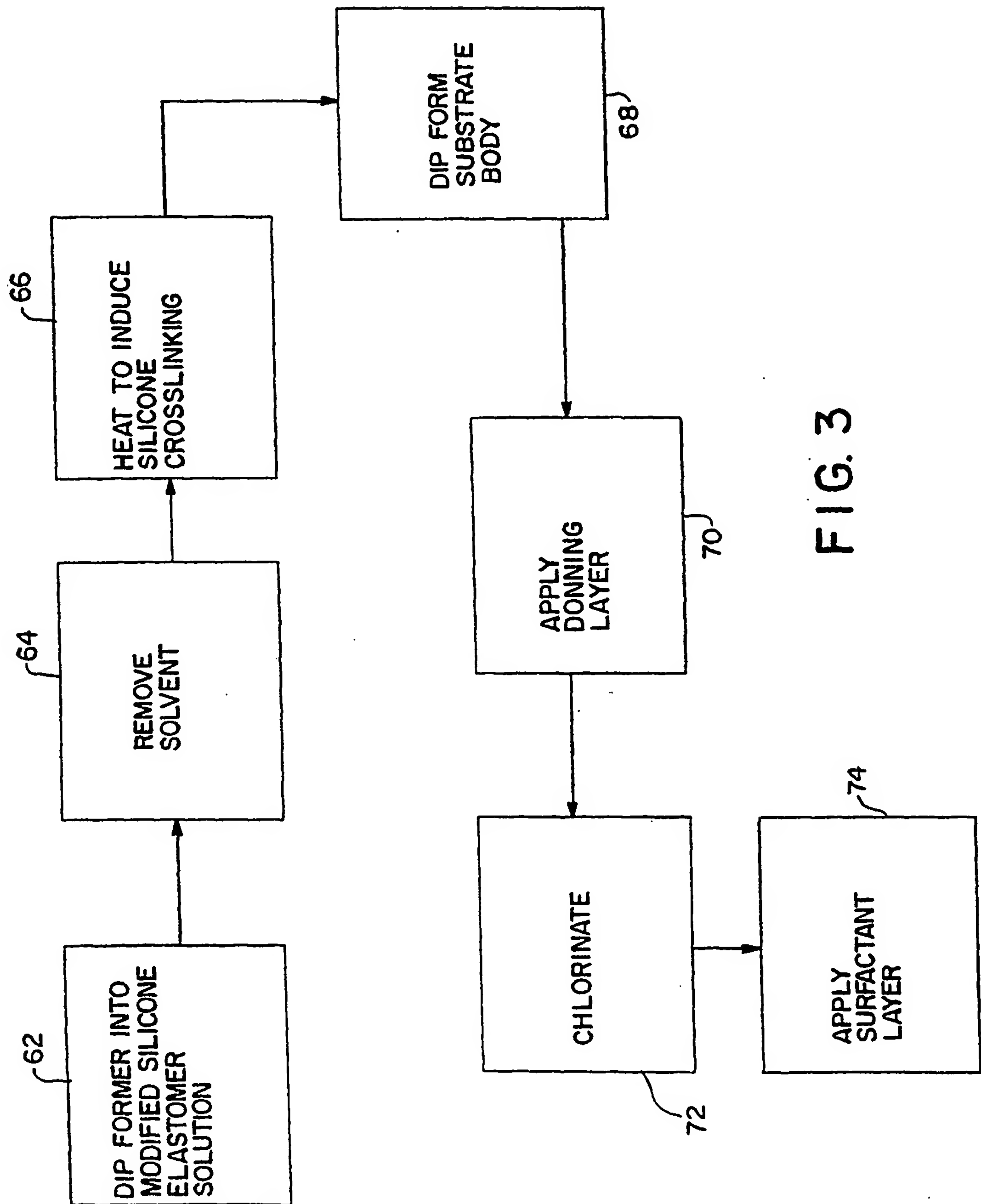


FIG. 3

## INTERNATIONAL SEARCH REPORT

Internatio pplication No

PCT/US 02/34149

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A41D19/00 C08J7/04 A61L31/10 A61L31/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A41D A61B A61L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 89 04647 A (STILLMAN SUZANNE) 1 June 1989 (1989-06-01)  claims 1,3,6,12,13,15,16 page 2, line 10 - line 24 page 4, line 1 - page 5, line 18 page 8, line 22 - line 25 examples 1,2	1-3, 5-11, 13-19, 22-24, 26-34, 36
A	US 5 706 522 A (BALLARINO DEBORAH E ET AL) 13 January 1998 (1998-01-13) claims 1-7 column 1, line 5 - line 10 column 3, line 42 - line 47 column 3, line 60 - line 65 column 4, line 7 - line 14  -/-	1-35



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

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- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

14 February 2003

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 302 852 A (JOUNG JOHN J)  1 December 1981 (1981-12-01)  claims 1,2,4,5,8-10,24,28,29  column 2, line 67 -column 3, line 15  column 3, line 45 - line 58  example 1</p> <p>-----</p>	1-35

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 02/34149

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US 5706522	A	13-01-1998	NONE		
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			EP	0035509 A1	16-09-1981
			WO	8100345 A1	19-02-1981
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